Problems of the Soot Formation in Exhausts of Internal Combustion Engines. Soot Abatement by Oxidation on Cu-Containing ZSM-5 Catalysts (Minireview)

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Abstract

Diesel engines are responsible for emission of particulate matters in industrial cities. Soot particles or particulate matters in diesel exhausts contain solid carbon, adsorbed organic compounds from the unburned fuel and products of its partial oxidation, as well as inorganic compounds, *e. g.*, sulphate ions, water and incombustible mineral residue. Soot has a strong affect on ecology in general and on human population health.

This minireview presents the information on the state of the art for soot removal from diesel exhausts, as well as the modern trends and recommendations. Soot particles can be removed from diesel exhausts using coagulation and precipitation methods, which do not have required efficiency. Application of soot filters with catalytic coating is known to be more effective. Pt-based catalytic washcoats ensure soot oxidation by oxygen at 550–650 °C. NO_x addition makes it possible to decrease the soot oxidation temperature to 300–400 °C over Pt catalysts and Cu-containing zeolites.

Key words: soot, diesel exhaust, diesel oxidation catalyst, Cu–ZSM-5

INTRODUCTION

In recent years, the content of harmful impurities in the air of big cities tends to increase due to the growth of traffic and number of cars. According to the data from Novosibirsk Municipal Committee on Environment and Natural Resources [1], the main sources of air pollution in Novosibirsk are automobile transport and power stations. The contributions of local boilers and industry are less significant. In 2014 the contributions of motor transport and power stations in the environmental pollution of the city were about 61 and 33 %, respectively [1]. Exhaust gases of vehicles mainly contained carbon monoxide (CO), hydrocarbons (CH) and nitrogen oxides (NO_x). Meanwhile, emissions from stationary sources were dominated by carbon black.

Toxic components, such as CO, hydrocarbons, NO and soot, are formed by incomplete fuel combustion under oxygen deficiency according to the following reactions:

$$CH_x + (0.5 + 0.25x)O_2 \rightarrow CO + 0.5xH_2O$$
$$CH_x \rightarrow C_6H_6 \ (C_8H_{18})$$
$$N_2 + xO_2 \rightarrow 2NO_x \text{ (at elevated pressure and temperature)}$$
$$CH_x + 0.25xO_2 \rightarrow C + 0.5xH_2O \ (H_2)$$

The contents of individual toxic compounds depend on the engine type, its operating conditions, fuel composition, and can be varied in a wide interval. Table 1 shows the compositions of exhausts from gasoline and diesel engines. Diesel engine exhausts contain 10 times less CO and 30 times less CH compared to gasoline engines. Therefore, for a long time diesel engines were considered to be more environmentally friendly. However, diesel engines produce higher

TABLE 1

Composition of automobile engine exhausts [2]

Parameters	Gasoline	Diesel
Average fuel consumption, kg/h	2.75	0.087
Total amount of exhaust gases (at 0 °C), m^3/h	28.95	0.914
N_2, vol. %	74−77	74−78
O_2, vol. %	0.3−8	2−18
H_2O, vol. %	3−5.5	0.5−9
CO_2, vol. %	5−12	1−12
Total amount of toxic compounds, vol. %	1−2	0.3
CO, ppm	5000−12 000	50−4000
CH, ppm	2000−30 000	90−3000
NO_x, ppm	100−8000	40−5000
SO_2, ppm	200	18−200
Particulate matter, g/m^3	0−0.04	0.1−1.1
Aldehydes, ppm	40	20
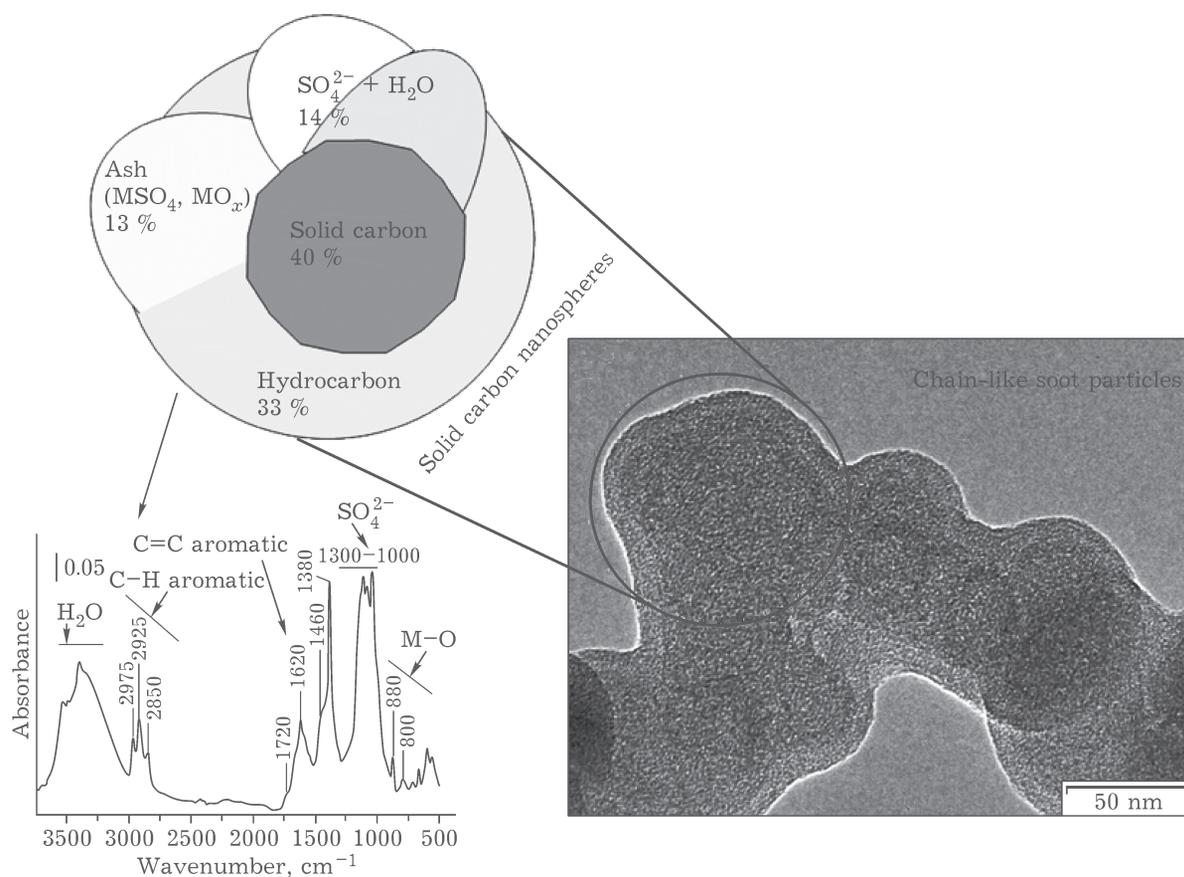
Fig. 1. Diesel soot particles: image and chemical composition.

emissions of soot particles. Their concentrations vary in the range of 0.1−1.1 g/cm^3, depending on the engine type and fuel composition [2]. It should be noted that diesel engines are responsible for 20 % of particulate matter emissions in industrial European cities [3] and up to 60 % in Russian cities [1].

The morphology, chemical composition and microstructure of diesel soot were comprehensively discussed in a number of scientific publications and summarized in several reviews [4−8]. So, here we shall very briefly outline its main characteristics. Diesel soot (Fig. 1) consists of microscopic solid carbon nanospheres with the size of 10−80 nm. Heavy hydrocarbons (paraffin, aromatic, oxygenated compounds and other soluble organic substances) from fuel and lubricant oil as well as some inorganic compounds, *e. g.* sulphate ions and water formed during the diesel fuel combustion, are adsorbed on their surface [4−9]. There is also incombustible mineral residue (ash) consisting of metal sulphates/oxides from engine corrosion, wear (Fe, Cu, Cr, Si, Al) and lube oil with additive package (Zn, Pb, P, S), and other small particulates [4−8]. These diesel soot nanoparticles agglomerate to form chain-like particles with the size of 0.1−1.0 μm (see Fig. 1) [4, 5].

Standards limiting the contents of toxic substances in exhausts of internal combustion engines have been accepted in the USA, California, Japan, and in the majority of European countries in the 1980s and 1990s. A Resolution of the Russian Federation government [10] on introduction of emission standards from Euro 2 (with December 10, 2005) to Euro 5 (January 1, 2014) in Russia was accepted in 2005. However, despite the adopted resolution [10], the Euro 5 standard on all Russian-made and imported cars is planned to be introduced in Russia only on January 7, 2016 [11]. Meanwhile, the Euro 6 standard is in effect in Europe since 2015. Emission standards for vehicles with diesel engines are presented in Table 2. Note that starting from the Euro 5 specification the soot content is limited to as low as 5 mg/km. At the same time the NO_x emissions should not exceed 0.18 g/km. There is a major contradiction of diesel purification systems, which propose to decrease the soot emissions by the temperature increase, which inevitably leads to higher NO_x concentration. Therefore, a solution is a compromise between the removal efficiency of soot and nitrogen oxides.

Catalytic converters for the purification of exhaust gases of automobile engines transforming toxic components into harmless gases were introduced in the 1970s. The first converters used Pt−Pd catalysts supported on alumina which only oxidized the HC and CO emissions [12]. Stricter NO_x standards in the 1980s led to development of three-way catalysts that simultaneously catalyze three types of reactions: CO and HC oxidation and NO_x reduction [12, 13]. In 1991, some European car manufacturers introduced vehicles with installed diesel oxidation catalyst (DOC) for reducing the soluble organic fraction, including polyaromatic hydrocarbons and aldehydes, in the particulate matter [14].

TABLE 2

Normative and technical documents limiting the content of toxic components in the exhaust of vehicles with diesel engines

Countries, emission standard	Year of coming into force				
	Euro 2	Euro 3	Euro 4	Euro 5	Euro 6
Europe	01.01.1996	01.01.2000	01.01.2006	01.01.2010	2015
Russia[a]	12.10.2005	01.01.2008	01.01.2010	01.01.2014	−
UNECE 49−02					
CO, g/km (g/kW · h)	1.0 (4.0)	0.64 (2.1)	0.5 (1.5)	0.5 (1.5)	0.5
CH, g/km (g/kW · h)	0.9 (1.1)	0.56 (0.66)	0.3 (0.46)	0.25 (0.46)	
NO_x, g/km(g/kW · h)	(7.0)	0.50 (5.0)	0.25 (3.5)	0.18 (2.0)	0.08 (1.8)
Particulate matter, g/km	0.1	0.05	0.025	0.005	0.005

[a]According to [10].

TABLE 3

Type, operation principle and efficiency of diesel particulate filters

Type	Operation principle	Efficiency	Disadvantage	Ref.
Centrifugal separators (traps)	Winding of gas flow and throwing off particulates to periphery due to centrifugal forces	Low efficiency that does not exceed 50 %	Highly dispersed particles with the size of 100−500 nm and concentration about 5−10 % are not trapped	[26−28]
Mechanical filters	Passing gas flow through the filter material. Filter materials are ceramics, wire mesh and fibrous materials.	High efficiency, reduce particulates in the size range of 15 to 500 nm by more than 90 %.	Filter creates back pressure at the engine exit. They become clogged with particulates and require regeneration at temperatures above 600 °C	[29−34]
Electric filters	Passing gas flow through electric field. Solid particles are deposited onto the precipitating electrodes	Up to 99.9 % at a low back pressure	The surface of electrode isolators soon becomes contaminated with soot. The efficiency depends on the engine operation mode.	[35−37]
Catalytic filters	Passing gas flow through a filter material with simultaneous soot trapping and oxidation. Wall-flow materials are porous SiC, cordierite, and other ceramics. Catalytic layers are based on Pt/CeO_2 and Pt/TiO_2	Up to 99.9 %	Filter is blocked with soot particulates, which are not oxidized at low exhaust temperatures. The catalyst provides passive regeneration and reduces the regeneration temperature below 500 °C. Deactivation by SO_2	[33, 34, 38−44]

The DOC catalyst adsorbs unburned hydrocarbons during the period when the emission gas temperature and catalytic activities are low. Then, it oxidizes the hydrocarbons as the emission temperature rises [2, 12]. However, the DOC catalyst does not oxidize soot in the particulate matter [14]. Conversion of particulates does not exceed 25−35 %. Requirements of Euro 4 and Euro 5 specifications for toxic compounds encourage purification systems to become multi-catalytic [15]. Now the main parts of the diesel purification system are diesel oxidation catalyst (DOC) [2, 12, 16−18], selective catalytic reduction catalyst (SCR) for NO_x removal [15, 19−25], and diesel particulate filter (DPF) [4−9, 14].

There are two major approaches to soot reduction in diesel engine exhausts.

The first approach is to decrease the soot formation during fuel combustion directly in the engine by an upgrade of the diesel engine, specifically fuel injection system, gas recirculation system, positioning of the oxidation catalytic converter close to the engine, etc. Improvement of the diesel fuel quality by adding H_2 and CO to the fuel, and by using other types of fuel, for example hydrogen, carbon monoxide, and biodiesel also allows automakers to abate the soot formation. Note that H_2 and CO can be produced from hydrocarbon fuel in an on-board catalytic reactor.

The second approach is to remove soot from the diesel exhausts by their filtration. A list of different filtration methods, their operation principles, efficiency and disadvantages are reported in Table 3. Soot can be removed from diesel exhausts using coagulation and precipitation methods [3, 4], which are considered to be slow and inefficient. Application of soot filters with catalytic coating is shown to be more effective (see Table 3). Moulijn *et al.* [45] wrote a comprehensive review on industrial diesel particulate filters and their perspectives. Fino *et al.* [46] reviewed the industrial developments in soot after-treatment systems by 2008.

Figure 2 demonstrates the design of a catalytic converter with a soot-oil separator devel-
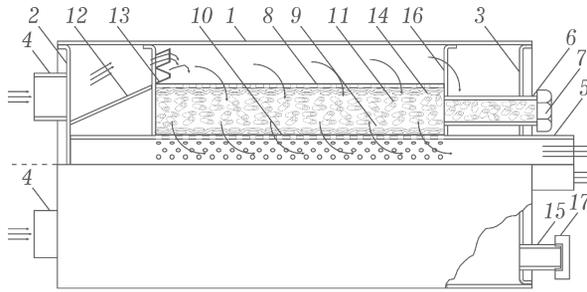
Fig. 2. Design of the catalytic converter with soot-oil separator [28]: *1* − steel casing, *2* − front reactor bottom, *3* − rear reactor bottom, *4* − inlet connection, *5* − outlet connection, *6* − loading pipe, *7* − drain plug, *8* − outer reactor tube, *9* − grid, *10* − perforated tube, *11* − Pt/Pd catalyst, *12* − reactor director, *13* − impeller, *14* − punch netting, *15* − air blast nozzle, *16* − partition, *17* − drain plug.

oped at BIC [28]. Exhausts enter the soot-oil separator where the particulate matter is separated from the gas due to the centrifugal force and are collected in the soot trap. The exhausts are filtered through a Pt (0.16 mass %), Pd (0.08 mass %)-alumina granulated catalyst bed where the toxic components (CO, CH, NO_x) are transformed into non-toxic compounds (CO_2, H_2O, N_2). These catalytic converters were tested at bench and on-road test runs during 1992−1994. The total run of the converters reached 90 000 km. In the mode including free acceleration and maximum idle running (Russian State Standard GOST 21-393−75), the post-treatment system with a supported Pt−Pd catalyst provided the diesel exhaust purification from CO, CH, and soot above 80, 80, and 50 %, respectively [28]. Most part of soot accumulated during 90 000 km of the on-road run was found to be located in the soot-oil separators. Some soot was also deposited on the external surface of the spent catalyst granules. The CHNS analysis and X-ray spectral fluorescence analysis demonstrated that the carbon and sulphur contents in the spent catalyst were about 0.8−1.1 and 0.4−0.8 mass %, respectively.
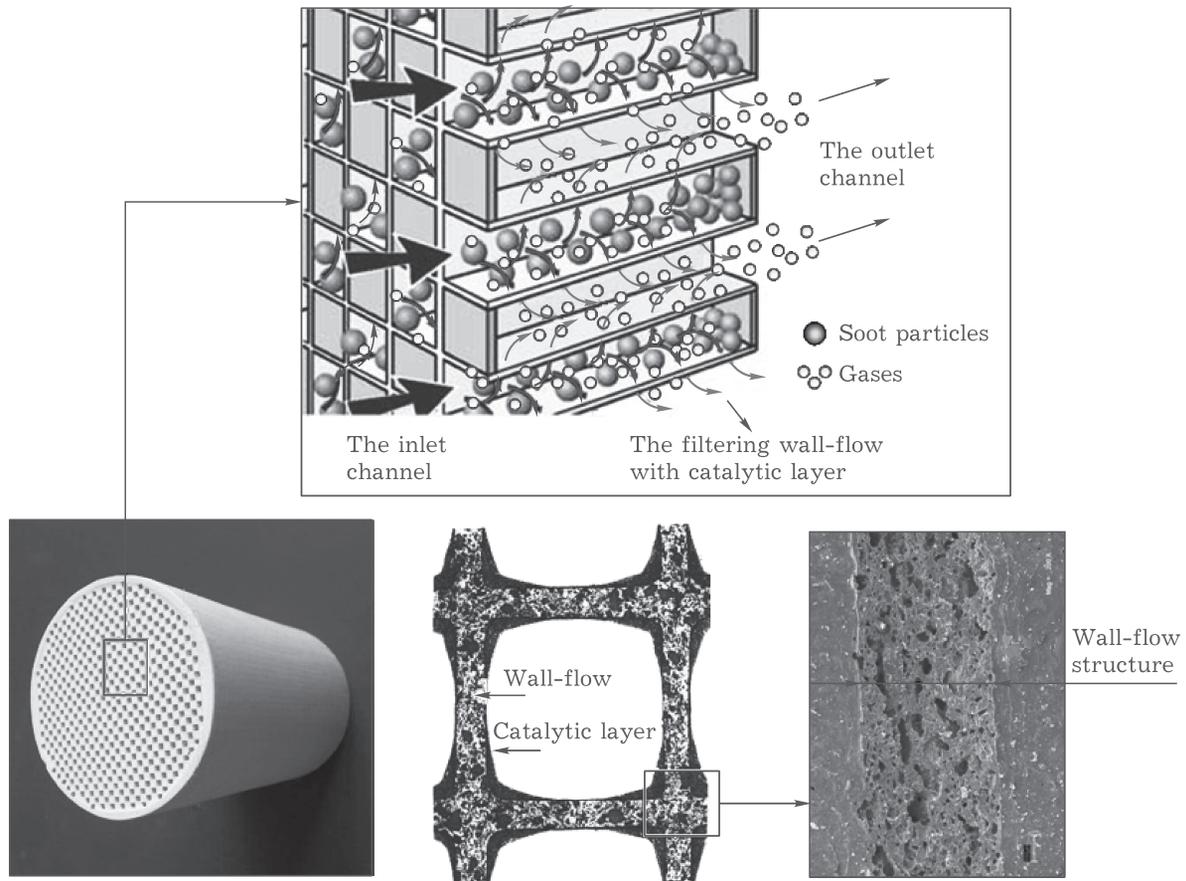
Fig. 3. Diesel particulate filter image and operation principle.

For the first time, "flow through monoliths" catalytic filters were proposed by Howitt and Montierth [47] and applied in 1988. These monolithic ceramic filters had open channels. The surface of the channels was covered by an alumina or silica washcoat with high surface area and small amount of Pt and Pd. These filters reduced the particulate matter emissions by oxidizing their soluble organic fraction together with hydrocarbons and CO. They reduced the particulate matter with the efficiency about $25-35 \%$, which was enough to comply with the past standards [48]. Moreover, the modern priority is to implement a system composed of a catalytic particulate filter and a NO_x removal system.

The current catalytic soot filter (Fig. 3) called wall-flow type filter is designed as a honeycomb monolith with alternating open and plugged channels [5–9, 45, 46]. The exhaust enters in a channel open at the inlet, filters through the porous channel wall and exits through an adjacent channel. During filtration soot is trapped in the inlet channels and deposited on their walls blocking them. These wall-flow filters can trap near $98-99$ mass % of the emitted particulate matter with a reasonable back-pressure. The filtering walls are made of porous silicon carbide (SiC), cordierite or aluminium titanate coated by a catalytic layer [38–46]. The porosity is precisely controlled during preparation using pore-forming additives and is about $45-50 \%$ [49]. The average pore radius is in the range of $10-20 \, \mu m$. Pt/CeO_2 and Pt/TiO_2 compositions [38–46], including these composition doped by Zr, La, and Pr cations [50–52], are most often suggested as catalytic materials. Sometimes, transition metals, such as Mn, Cu, Cr, Co, are considered as the active component [45, 52]. They are cheaper than noble metals but less active in soot oxidation [52].

A trademark technology "continuously regenerating trap" was developed and commercialized by Johnson Matthey [38–40, 53]. This system utilizes oxidation of soot collected on the DPF with NO_2 by converting NO to NO_2 over a Pt-coated monolith. NO_2 is known to be a much better oxidant than O_2. As a result NO_2 oxidizes soot at lower temperature compared to oxygen ($300-400 \, ^{\circ}C$ vs. $550-650 \, ^{\circ}C$). This process involves the following reactions: $NO_2 + C = CO + NO$ and $CO + NO + O_2 = NO_2 + CO_2$.

Passive regeneration is successful when the engine operates in the maximum load mode. However, during driving in the city the exhaust temperature is insufficient, and the soot is intensively deposited on the filter walls clogging him. This is the main disadvantage of catalytic filters. In this case, active regeneration is required. It is based on soot oxidation to carbon dioxide by O_2 over $Pt-TiO_2$ or $Pt-CeO_2$ catalytic washcoats. Active regeneration requires about 10 min at $600-650 \, ^{\circ}C$. This system provides near 90 % decrease of particulate matter emissions.

A technology of an exhaust purification to Euro 4 using higher rates of a externally cooled exhaust gas recirculation (EGR) with the particle reduction technology PM-Kat was developed and patented by MAN Nutzfahrzeuge [54]. Here, about 20 % of exhausts is selected from the main stream, cooled to $200 \, ^{\circ}C$, and again mixed with the air coming to the engine. The exhaust gas recirculation is designed to decrease the maximum combustion temperature and form smaller quantities of NO_2. The particulate filter contains a corrugated metal trap and an oxidizing catalytic converter. The soot is accumulated in the corrugated metal trap due to induced turbulence. The oxidizing catalytic converter provides NO oxidation to NO_2 over catalytically active Pt particles. Carbon reacts with NO_2 created at the first purification stage with the formation of CO_2 and NO. The separation rate of the solid matter microparticles is claimed to be 60 % overall. Chemical processes proceed in PM-Kat without consumption of external energy. This is an open filter design. So, soot clogging does not create pressure drop. However, when the filter is filled by soot, the exhaust gases are not cleaned from soot at all.

Toyota developed and employed from 2003 a diesel particulate-NO_x reduction (DPNR) system as a post-treatment technology aimed at simultaneous reduction of particulate matter and NO_x [55–57]. This system used the NO_x storage and reduction catalyst.

So, soot particles do not interact with oxygen from the air at temperatures below $600 \, ^{\circ}C$ [4], whereas typical diesel engine exhaust temperatures fall within the $200-500 \, ^{\circ}C$ range [9, 12, 44] due to the low content of CO and CH [2]. Therefore, an oxidation catalyst is necessary to increase the oxidation rate of soot particles at low temperatures. This catalyst must

be efficient in order to oxidize soot and regenerate the diesel particulate filter continuously, since the soot accumulation could lead to an increase in the pressure drop and engine malfunction. The catalyst should be thermally stable because the temperature inside the DPF can increase up to ca. 1000 °C due to the highly exothermal soot combustion reaction. For Euro 5 and Euro 6, a catalyst ensuring the removal of NO and soot at the same time is attractive. In the modern exhaust post-treatment systems, the removal of soot and NO_x are performed by two modules: DPF coated by Pt-based catalysts and $DeNO_x$ reactor with Pt,Rh-based or MnO_x/CeO_2–TiO_2-containing catalysts. In this regard, copper-substituted zeolites are promising. The interest of researchers to Cu-substituted zeolites (ZSM-5, SSZ-13, *etc.*) is caused by prospects for their use in systems for diesel exhaust purification from nitrogen oxides by selective reduction by ammonia [58, 59] and hydrocarbons [19, 24, 25]. The activity of Cu-ZSM-5 catalysts in these reactions depends non-linearly on the copper content due to the difference in the electron state of copper cations. $DeNO_x$ reactivity was found [19, 24, 25] to correlate with the growth in the number of the isolated Cu^{2+} ions and Cu structures with extra-lattice oxygen. Meanwhile, the reactivity decreases when the content of copper-oxide clusters on the external surface of the zeolite increases [25].

In this communication, some correlations between the structure of catalytically active Cu–ZSM-5 centers containing isolated Cu^{2+} ions, structures of Cu^{2+} ions with extra-lattice oxygen, clusters and nanoparticles of CuO, and their reactivity in the soot oxidation by oxygen and promoted by nitrogen oxides will be discussed. Precipitation of soot particles on the external surface of Cu-ZSM-5 crystallites can lead to catalyst deactivation due to blocking of catalytically active centers. Soot inflammation can lead to a change in the structure of the active centers as a result of their overheating.

EXPERIMENTAL

Soot characterization

The specific surface area (S_{BET}) was calculated with the Brunauer–Emmett–Teller (BET)
method using nitrogen adsorption isotherms measured at the liquid nitrogen temperature with an automatic Micromeritics ASAP 2400 sorptometer.

Powder XRD measurements were performed with a HZG-4C diffractometer using the monochromatic CuK_α ($\lambda = 1.5418$ Å) radiation.

HRTEM images were obtained using a JEOL JEM-2010 electron microscope with a lattice-fringe resolution of 0.14 nm at the accelerating voltage of 200 kV. High resolution images of periodic structures were analyzed by the Fourier method. Before measurements the samples were prepared by ultrasonicating a small quantity of the powder in ethanol for several minutes. The resultant slurry was then deposited on perforated carbon films mounted on copper grids.

IR spectra were recorded with a Cary 660 FTIR spectrometer (Agilent Technologies) within the range of $4000-250$ cm^{-1} at 4 cm^{-1} resolution in the Attenuated Total Reflectance mode using a GladiATR unit. The spectra of the catalysts were measured without using diluents.

The thermal analysis was carried out with a NETZSCH STA 449C apparatus in the temperature range from 20 to 800 °C at the heating rate of 10 °C/min in air. The accuracy of determining the mass losses and temperature was 0.5 % and 5 %, respectively.

Catalyst preparation

Cu–ZSM-5 samples were prepared by the ion exchange of parent H–ZSM-5 (Si/Al = 17) with aqueous and ammonia solutions of copper acetate, which had the NH_4^+/Cu^{2+} molar ratio equal to 0, 3, 6, and 30 and pH close to 5.7, 9.5, 10.5, and 11.5, respectively. Copper concentrations in solution were 5 g Cu/L. Ammonia solutions of copper acetate were prepared by addition of an ammonia solution to an aqueous copper acetate solution. The slurry concentration (the ratio of the solution volume to the zeolite mass, S/Z) was 10. After 48 h of the ion exchange at room temperature, the zeolite samples were filtered and washed with distilled water or ammonia solution with pH 10.5. All the samples were dried at 110 °C and calcined in air at 500 °C. According to ESR, UV-Vis DR and H_2-TPR, the main copper state in the calcined Cu–ZSM-5 catalysts prepared at

the NH_4^+/Cu^{2+} molar ratio equal to 0 and 30 were isolated Cu^{2+} ions in cation exchange sites. At $NH_4^+/Cu^{2+} = 6$ the structures of Cu^{2+} ions with extra-lattice oxygen in zeolite channels predominated. Finally, at $NH_4^+/Cu^{2+} = 3$ CuO nanoparticles located on the external surface of zeolite crystallites were the main form of copper [25]. Here the catalysts are referred to as xCu(y)-ZSM-5-z, where x is the copper loading in mass %, y is the NH_4^+/Cu^{2+} molar ratio in copper-ammonia solution used for the catalyst preparation, z is the Cu^{2+}/Al^{3+} atomic ratio in the catalyst, and ZSM-5 is the zeolite type.

Catalyst characterization

Oxidation of soot from diesel engines was conducted in the temperature programmed oxidation (TPO) mode. A mixture of the catalyst and soot (90/10) was thoroughly mixed to achieve close contact between their particles. A sample containing 0.3 g (0.5 cm^3) of the mixture as 0.25−0.5 mm grains was loaded into a quartz tubular reactor. Then a gas mixture containing 10 vol. % O_2 in Ar (test 1) or 10 vol. % O_2 with 450 ppm NO in Ar (test 2) with a space velocity of 36 000 h^{-1} was supplied into the reactor. The sample was heated from 50 to 700 °C with a 10 °C/min rate. The catalyst bed temperature was monitored by a chromel-alumel thermocouple placed coaxially and internally in the middle of the catalyst bed, making it possible to measure the temperature with ±1 K precision. A continuous gas analyzer TEST-1

equipped with electrochemical sensors was used for the analysis of the gas mixture components (CO_2, CO, O_2, NO, and NO_2).

Additionally, the catalyst activity in NO oxidation to NO_2 (test 3) was measured in the temperature programmed reaction mode under the same conditions over the catalyst load without the soot (270 mg).

Pulse NO addition to the gas mixture (test 4) was used to prove that NO promotes the soot oxidation. The catalyst/soot mixture (270/30 mg) was loaded in the tubular quartz reactor, and a mixture of 10 vol. % O_2 in Ar was fed to the reactor. After stabilization of the CO and CO_2 emissions, 3.6 μmol NO was injected into the reactor as a mixture of 0.35 vol. % NO in Ar for 2 min, and surplus CO and CO_2 emissions were measured. These measurements were carried out isothermally in the 300−500 °C temperature range with ~25 °C increment.

To study the thermal stability fresh and spent Cu−ZSM-5 catalysts were tested in selective reduction of NO with propane in the oxygen presence proceeding according to the following reaction equation:
$$2NO + C_3H_8 + 4O_2 = N_2 + 3CO_2 + 4H_2O$$
Their catalytic activity was studied using a fixed-bed flow reactor made from quartz and heated by an electrical oven. The reactor temperature was monitored by a chromel-alumel thermocouple placed coaxially and internally in the middle of the catalyst bed. The compositions of the feed and reaction products were determined with a TEST-1 analyzer with the
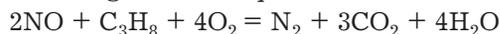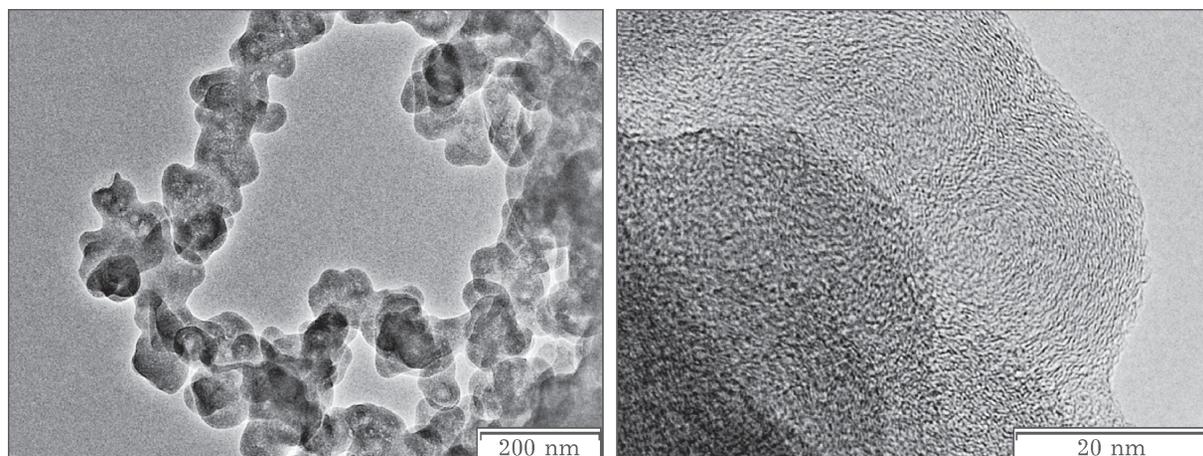
Fig. 4. TEM images of diesel soot particles accumulated in the soot-oil separator during on-road test with KAMAZ trucks.

precision of 5 ppm for NO, 5 ppm CO, 0.005 vol. % for C_3H_8 and 0.1 vol. % for O_2. The catalytic activity was measured in the temperature range of 200−550 °C with the gas flow rate 42 000 h^{-1}. The catalyst was mixed with 1−2 mm quartz particles in a 1 : 1 ratio. The catalyst volume was 0.5 cm^3. The feed consisted of 340 ppm NO, 0.15 vol. % C_3H_8, 3.1−3.2 vol. % O_2, and Ar balance. The catalytic activity was characterized as NO conversion (X, %) at desired temperature.

RESULTS AND DISCUSSION

Diesel soot properties

In our catalytic experiments we used automobile soot that was accumulated in the soot and oil separators (centrifugal cyclones) of the diesel exhaust post-treatment system with supported Pt and/or Pd catalysts during on-road tests with KAMAZ trucks [28]. Soot particles in diesel exhausts (the so-called particulate matter) are different both by the composition and microstructure from commercial soot samples (for example, Printex-U). As a result they have different physicochemical properties and reactivity. Firstly, in addition to solid carbon, the diesel soot contains high amounts of adsorbed volatile organic compounds from the unburned fuel and products of its partial oxidation, which makes its ignition easier [4−8]. Printex-U contains higher percentages of fixed carbon and lower percentages of volatile matter, ash and
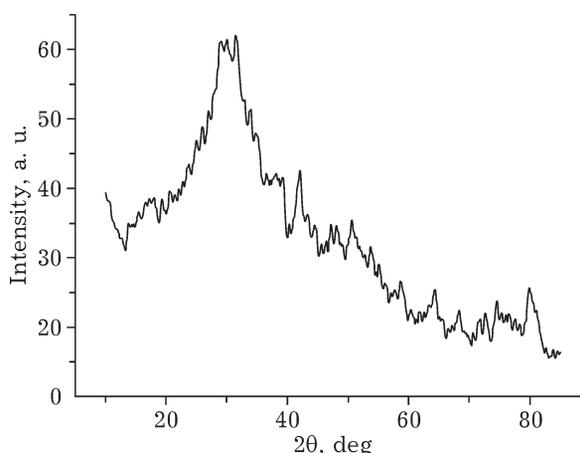
Fig. 5. XRD of diesel soot particles accumulated in the soot-oil separator during on-road test with KAMAZ trucks.

wetness than the real diesel soot [5, 6]. Secondly, the diesel soot also contains some inorganic compounds, *e. g.*, sulphate ions, water and mineral incombustible residue (ash) [7−9].

Our diesel soot sample was first characterized by various methods. According to our CHNS analysis, the contents of carbon, sulphur and nitrogen in the diesel soot accumulated in the soot-oil separators were 56, 1.7 and 2.4 mass %, respectively. According to the X-ray fluorescence analysis, the soot also included mineral compounds containing (mass %): P 0.04, Pb 0.006, Fe 1.4, Si 0.11, and Al 2.1. The diesel soot sample had the specific surface area of 23 m^2/g determined from the nitrogen adsorption/desorption isotherms. A TEM image (Fig. 4) showed that the diesel soot consisted of nanos-
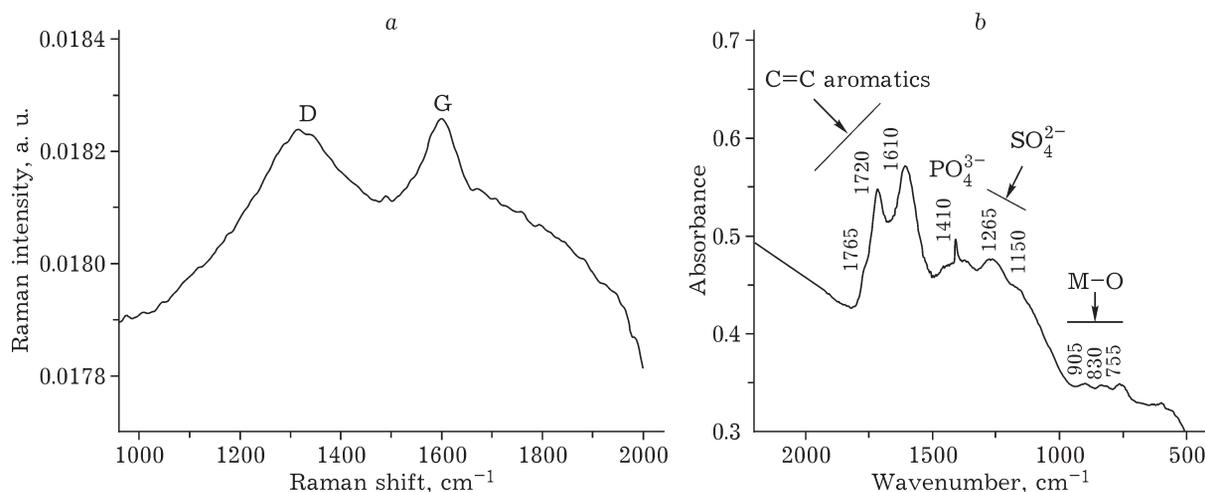
Fig. 6. Raman (*a*) and FTIR (*b*) spectra of diesel soot particles accumulated in the soot-oil separator during on-road test with KAMAZ trucks.
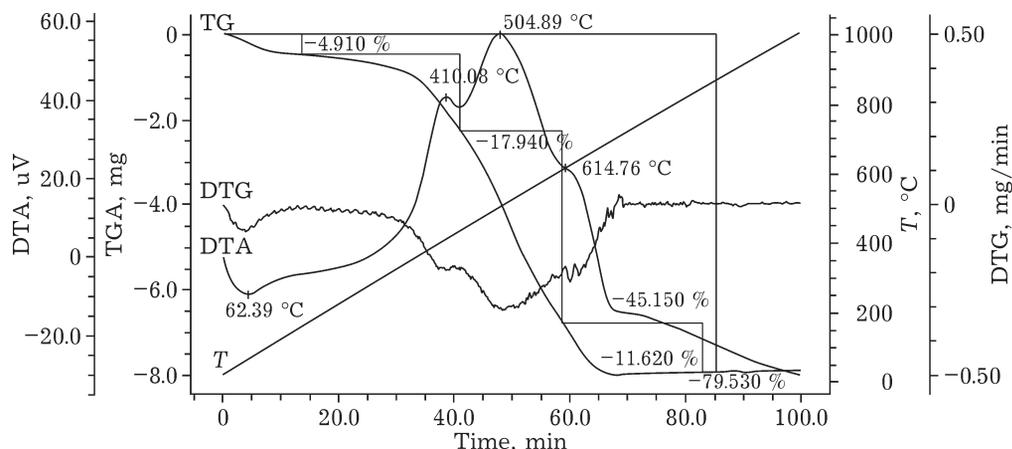
Fig. 7. TG, DTG, DTA curves of diesel soot particles accumulated in the soot-oil separator during on-road test with KAMAZ trucks.

cale particles with a size of 50−70 nm comprised of solid carbon having amorphous structure with graphite-like layers observed by XRD (Fig. 5) and Raman spectroscopy (Fig. 6, *a*). Aromatic compounds on the surface of the soot particles and characterized by adsorption bands in the range of 1620−1765 cm^{-1} were detected by FTIR (see Fig. 6, *b*) in addition to some inorganic compounds (SO_4^{2-}, 1265 and 1150 cm^{-1}, and PO_4^{3-}, 1410 cm^{-1}). The thermal analysis (Fig. 7) illustrated that the main part of the soot sample from the diesel engine exhaust burned in the air in the temperature range from 415 to 600 °C. The ash content was ca. 20 %. So, the diesel soot combustion occurred at temperatures lower by 50−100 °C than those of commercial samples [8] for both the catalytic and non-catalytic cases.

Soot abatement by oxidation on Cu-containing ZSM-5 catalysts

We used four Cu-containing ZSM-5 catalysts characterized by different oxidation properties due to different states of copper ions: isolated Cu^{2+} ions, structures of Cu^{2+} ions with extra-lattice oxygen, and CuO nanoparticles. The first copper state predominated in the catalysts 0.7 % Cu(*0*)−ZSM-5-*0.15* and 1.8 % Cu(*30*)-ZSM-5-*0.38* with the copper content differing by a factor of three. The second state predominated in the catalyst 2.8 % Cu(*6*)-ZSM-5-*0.59* prepared by ion-exchange with copper-ammonia solution with NH_4^+/Cu^{2+} equal to 6. The third state was the main state in the catalyst 3.8 % Cu(*3*)−ZSM-5-*0.80*.

The results of soot oxidation by oxygen-containing mixtures with and without the NO admixture are presented in Fig. 8. A number of conclusions can be drawn. First, the soot gradually burns out over the Cu-zeolite catalysts in a wide temperature range, 420−700 °C (see Fig. 8, *a*, curves *3–6*) instead of 470−520 °C on quartz (see Fig. 8, *a*, curve *1*). This proves that temperature can be decreased to prevent the local overheating of the catalytic bed. Second, the NO addition to the oxygen-containing mixture promotes the soot oxidation (see Fig. 8, *b*) due to soot interaction with NO_2 formed under the reaction conditions as shown by the reaction equation: $NO_2 + C = CO + NO$. Note that NO_2 was present in trace amounts (40−50 ppm) in the final reaction mixture. Special experiments (without soot) showed that NO is oxidized to NO_2 over Cu-containing catalysts at lower temperatures than in the absence of the catalyst and the zeolite, near 200−400 °C versus 515 and 460 °C. The NO_2 concentration depended on the catalyst composition and changed from 150 to 300 ppm. Third, a correlation of the catalytic activity of the Cu-containing zeolites with the structure of their catalytically active centers showed that the structures of Cu^{2+} ions with extra-lattice oxygen in the zeolite channels and square-planar clusters $(Cu_2O_2)_x$ on the surface of zeolite crystallites (catalyst 2.8 % Cu(*6*)−ZSM-5-*0.59*, see Fig. 8, *b*, curve *5*) are more active compared to isolated Cu^{2+} ions (catalyst 0.7 % Cu(*0*)−ZSM-5-*0.15*, see Fig. 8, *b*, curve *3*) and CuO nanoparticles (catalyst 3.8 % Cu(*3*)−ZSM-
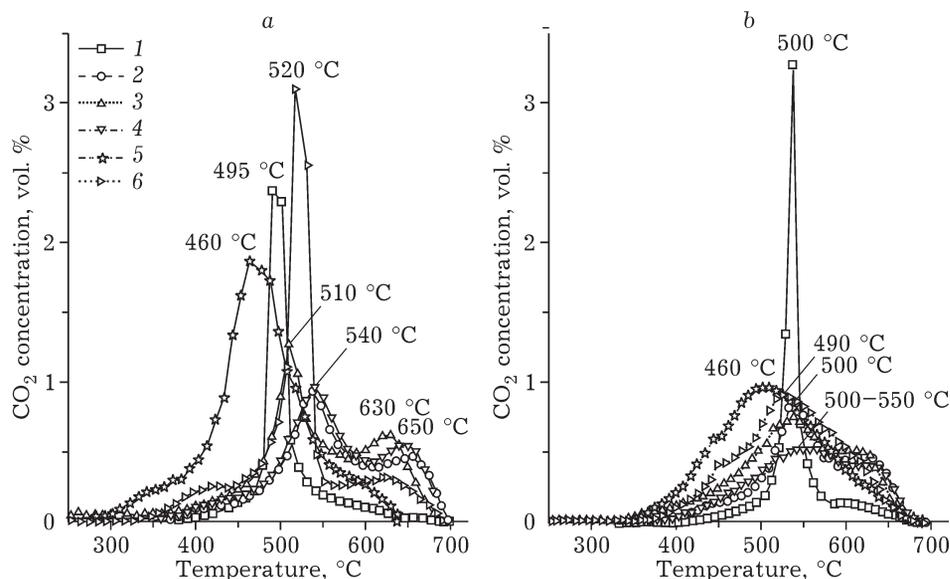
Fig. 8. Temperature plot of CO_2 evolution during catalytic oxidation of automobile soot in the TPO mode by oxygen (a, 10 vol. % O_2 in Ar) and oxygen with NO (b, 10 vol. % O_2 and 450 ppm NO in Ar): 1 – quartz, 2 – H-ZSM-5, 3 – 0.7 % Cu(0)–ZSM-5-0.15 with isolated Cu^{2+} ions, 4 – 3.8 % Cu(3)-ZSM-5-0.80 with CuO nanoparticles, 5 – 2.8 % Cu(6)–ZSM-5-0.59 with structures of Cu^{2+} ions having extra-lattice oxygen, and 6 – 1.8 % Cu(30)-ZSM-5-0.38 with isolated Cu^{2+} ions; soot concentration is 10 mass %; temperature increase rate is 10 °C/min.

5-0.80, see Fig. 8, b, curve 6). As a result, the catalyst 2.8 % Cu(6)–ZSM-5-0.59 has lower starting temperature of NO-promoted soot oxidation (460 °C), ensures higher soot conversion (90–95 %) and lower concentration of the formed CO (at more

50 ppm) in comparison with the other catalysts (Table 4). The catalyst 2.8 % Cu(6)–ZSM-5-0.59 possesses the best catalytic behaviour in NO oxidation to NO_2 providing 30 % NO conversion at 185 °C and 67 at 400 °C when the catalyst was without soot.

TABLE 4

Results of temperature-programmed soot oxidation by oxygen and oxygen with NO over different catalysts

No.	Catalyst	Cu main state	Soot oxidation by oxygen		Soot oxidation by oxygen with NO (400 ppm)			
			T_{max}, °C	XC, %	T_{max}, °C	XC, %	CCO, ppm (T_{max}, °C)	CNO, ppm
1	Quartz	–	495–505	75	505	75	12000 (510)	35–50
2	H–ZSM-5	–	540, 660	57	505	57	1700 (530)	30–60
3	0.7 % Cu(0)–ZSM-5-0.15	isolated Cu^{2+} ions	510, 630	75	505	75	150 (270)	10–35
4	3.8 % Cu(3)-ZSM-5-0.80	CuO nano-particles	540, 630	62	530–550	62	100 (500)	30–80
5	2.8 % Cu(6)–ZSM-5-0.59	structures of Cu^{2+} ions with extra-lattice oxygen	460	95	460	93	50 (200–600)	20–40
6	1.8 % Cu(30)-ZSM-5-0.38	isolated Cu^{2+} ions	510, 630	86	490	86	170 (500)	10–40

Note. T_{max} is temperature at which maximum soot conversion is observed; XC is total soot conversion; CCO is maximum concentration of carbon monoxide in the reaction product and temperature of its formation; CNO is maximum concentration of nitrogen dioxide in the reaction product.
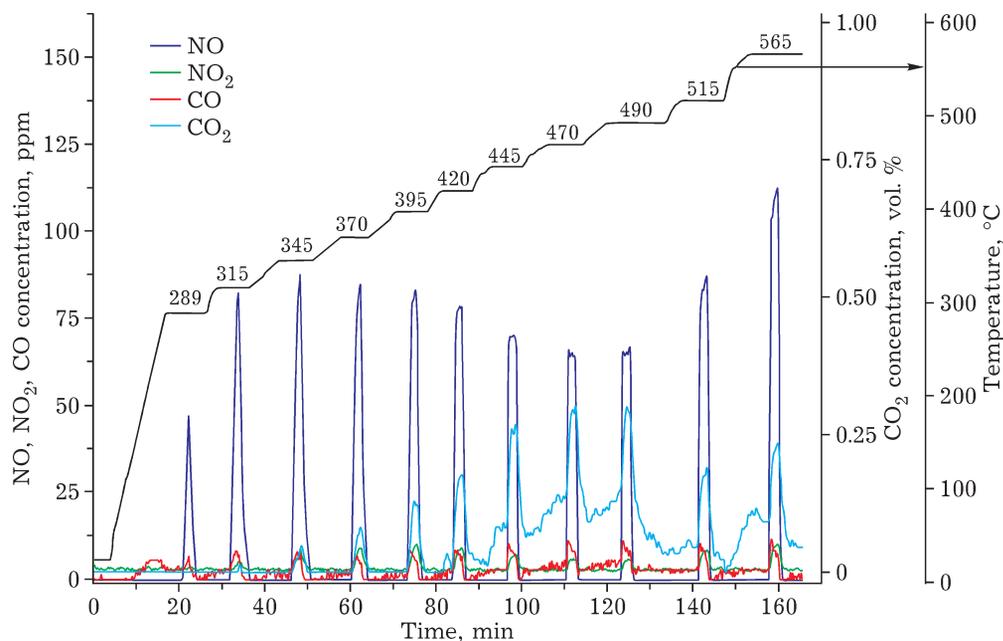
Fig. 9. NO, NO$_2$, CO, and CO$_2$ concentrations over the catalyst 2.8 % Cu(*6*)−ZSM-5-*0.59* with structures of Cu^{2+} ions having extra-lattice oxygen during test of soot oxidation by oxygen with NO pulses.

The same result was obtained in the NO pulse mode. A typical pattern of CO$_2$, CO, NO, and NO$_2$ evolution over the catalyst 2.8 % Cu(*6*)−ZSM-5-*0.59* upon NO injection into O$_2$ (10 vol. %) in Ar stream in the temperature range of 285−565 °C is shown in Fig. 9. The NO pulse results in the NO oxidation to NO$_2$ and soot oxidation to CO and CO$_2$. Significant concentrations of CO$_2$ are registered already at 315 °C and reach a maximum at 445−490 °C. The number of NO recycles for the catalyst 2.8 % Cu(*6*)-ZSM-5-*0.59* − soot mixture varied from 2 to 40 with temperature increasing from 315 to 445 °C. For the catalyst 0.7 % Cu(*0*)-ZSM-5-*0.15* with isolated Cu^{2+} ions, the numbers are lower in agreement with the lower activity in NO to NO$_2$ oxidation. Over 0.7 % Cu(*0*)-ZSM-5-*0.15* the soot oxidation promoted by NO begins at 340 °C, the number of NO recycles varies from 1 to 30 in the temperature range of 340−440 °C. Apparent activation energy of soot oxidation calculated on the basis of temperature dependences of NO to NO$_2$ recycling was found to be near 95−115 kJ/mol. This value is slightly higher than the one published for Pt-containing catalysts (50−75 kJ/mol) [60−62]. The difference is explained by lower activity of Cu−ZSM-5 catalysts in the NO oxidation to NO$_2$.

Since the soot oxidation reaction is highly exothermal, the catalyst can overheat up to temperatures as high as 1000 °C during the DPF regeneration. At such temperatures the copper active centers in the Cu−ZSM-5 catalyst can be changed due to sintering of the copper species and destruction of the zeolite lattice. As a result, DeNO$_x$ properties of Cu−ZSM-5 catalysts will worsen. Therefore, we decided to study the catalytic behaviour of fresh and spent Cu−ZSM-5 catalysts in SCR of NO by propane. This reaction allows us to remove NO from diesel exhausts. The results of NO SCR by propane are shown in Fig. 10 as NO conversion vs. temperature.

In the temperature range of 200−550 °C, the main products of NO reduction by propane over Cu−ZSM-5 catalysts were N$_2$, CO$_2$, CO and H$_2$O. The NO conversion grows with temperature and reaches 99.5 % at 320 °C over the fresh 2.8 % Cu(*6*)−ZSM-5-*0.59* catalyst. Then it remains virtually constant up to 450 °C (see Fig. 10, *a*, curve *1*). The propane conversion also increases with temperature and reaches 98 % at 345 °C (see Fig. 10, *b*, curve *1*). The same NO transformation characteristics are also observed for the spent catalysts. Their temperatures of 50 % conversion vary in a narrow temperature range from 277−283 °C (see Fig. 10, *a*,
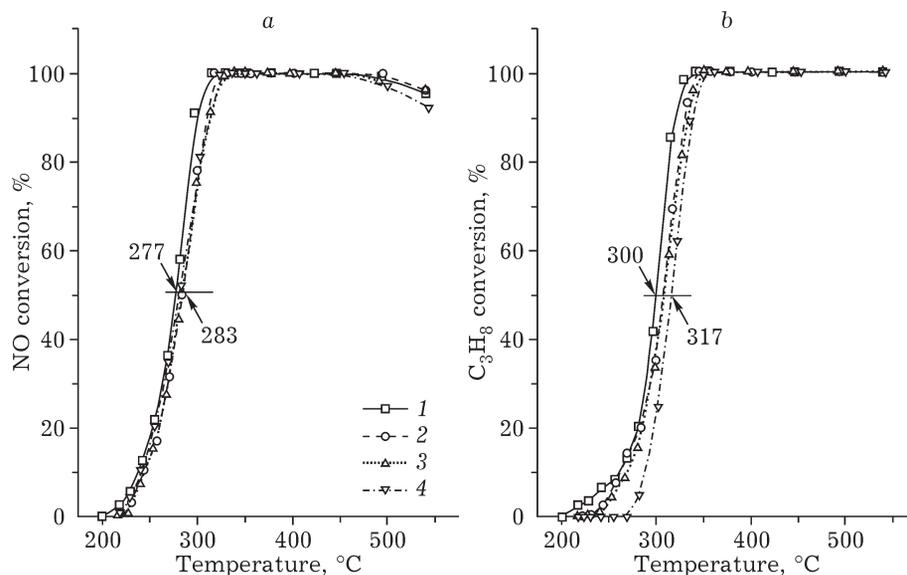
Fig. 10. NO (*a*) and propane (*b*) conversion over the catalyst 2.8 % Cu(*6*)−ZSM-5-*0.59* with structures of Cu^{2+} ions having extra-lattice oxygen, fresh sample (*1*) and samples after soot TPO by oxygen (*2*), soot TPO by oxygen with NO (*3*), and soot oxidation by oxygen with NO pulses (*4*).

curves *2*−*4*). The oxidizing ability of the spent catalyst 2.8 % Cu(*6*)−ZSM-5-*0.59* changes slightly more. For example, the temperature of 50 % propane conversion increases from 300 °C to 307−317 °C. The catalyst tested in the NO pulse mode has the highest temperature of 50 % propane conversion ($T_{50\,\%}(C_3H_8) = 317$ °C). This is probably related to the presence of soot residues in the catalyst, which block the access of propane to the catalytically active Cu centers.

The activation energy calculated from the NO and C_3H_8 conversion rates in the Arrhenius coordinates for the fresh and spent catalysts did not change much and was equal to 120−135 kJ/mol for NO transformation and 120−130 kJ/mol for C_3H_8 transformation.

Since the catalyst did not lose its activity in selective reduction of nitrogen oxides by propane, we concluded that the structure of the catalytically active centers in the catalyst 2.8 % Cu(*6*)−ZSM-5-*0.59* was not changed during the temperature-programmed soot oxidation reactions (see Fig. 8), at least during a single run of the soot oxidation procedure. This assumption was confirmed by the UV-Vis DR and ESR data.

Cu-containing zeolites combine good soot oxidation activity with unique $DeNO_x$ behaviour. Their characteristics depend on the copper electronic state. The Cu−ZSM-5 catalysts containing copper structures with extra-lattice oxygen possess the most promising properties for diesel soot oxidation.

CONCLUSIONS

In this review, we summarized the available information about the problem of the soot formation in exhausts of diesel engines and methods for its solution.

The leading manufacturers of diesel exhaust purification systems recommend application of diesel particulate filters with a catalytic coating as a more effective alternative to coagulation and precipitation. Pt−CeO$_2$ and Pt−TiO$_2$ catalysts coated on the DPF walls significantly decrease the soot ignition temperature to approximately the diesel exhaust temperatures. However, Pt and other noble metals are expensive and sensitive to sulphur poisoning. With tremendous progress achieved in Pt-based catalysts, there are still many challenges to development of better soot oxidation catalysts.

Cu-containing zeolites are candidate catalytic materials for DPF. The Cu−ZSM-5 catalysts combine good soot oxidation activity with unique $DeNO_x$ properties. The Cu−ZSM-5 catalyst formulation and especially the copper electronic

state was shown to play a significant role in soot oxidation, as well as $DeNO_x$ behaviour. Soot oxidation by oxygen with NO over Cu−ZSM-5 catalyst having the structure of Cu^{2+} ions with extra-lattice oxygen takes place at low combustion temperatures with high selectivity to CO_2.

The design of multi-component catalysts and the control of the catalyst morphology are promising trends for developing advanced soot oxidation catalysts with high oxidation activity, high thermal stability, and long life-time.

Acknowledgement

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Проблемы образования сажи в отработанных газах двигателей внутреннего сгорания. Удаление сажи окислением на Cu-содержащих ZSM-5 катализаторах (обзор)

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Аннотация

Дизельные двигатели выбрасывают с продуктами сгорания в атмосферу частицы сажи, что наиболее критично для экологии промышленных городов. Сажа или твердые частицы, выбрасываемые вместе с отработанными газами дизельных двигателей, содержат твердый углерод, адсорбированные органические соединения из несгоревшего топлива и продуктов его парциального окисления, а также неорганические вещества, такие как сульфат-ионы, вода и несгораемый минеральный остаток.

В данном обзоре рассмотрены способы удаления частиц сажи из отработанных газов дизельных двигателей, а также проанализированы современные тенденции и рекомендации. Сажа может быть удалена из отработанных газов дизельных двигателей путем процессов коагуляции и осаждения, которые, однако, не обеспечивают требуемую эффективность очистки. Использование сажевых фильтров с каталитическим покрытием является более эффективным способом удаления сажи из отработанных газов. Каталитические покрытия на основе Pt-содержащих композиций обеспечивают окисление сажи при 550−650 °C. Добавление NOx в отработанные газы позволяет снизить температуру окисления сажи до 300−400 °C на Pt-катализаторах и Cu-содержащих цеолитах.

Ключевые слова: сажа, отработанные газы дизельных двигателей, катализатор окисления для отработанных газов дизельного двигателя, Cu−ZSM-5